

SULFUR OXIDE SORPTION WITH LAYERED CHLORITE-TYPE CONTACT SOLIDS

FIELD OF THE INVENTION

The present invention relates to sorbents useful in sulfur abatement.

BACKGROUND OF THE INVENTION

Industry is lacking an economic and effective sorbent composition such as fluidized bed catalyst or additive contact solids for economically removing sulfur oxides from emissions from a variety of industrial processes. Further, the industry lacks effective and economical methods for using a fluidized bed of particles to remove sulfur oxides from emissions.

A structural description of the class of "brucite" crystals is found in the work of Pinnavaia et al (U.S. Patent No 5,358,701, incorporated by reference). Briefly, the metal oxide layers consist essentially of magnesium oxide (magnesia, MgO) configured structurally with octahedral hydroxy groups. A trivalent metal oxide, such as alumina (Al_2O_3), can be inserted into the brucite crystalline lattice in the octahedrally-coordinated metal oxide layer. Some of these brucitic materials are known as sorbents per se (see U.S. Patent No. 5,928,496). Other brucitic materials are known as binders for sorbent contact solids.

SUMMARY OF THE INVENTION

It has been discovered that magnesia-rich phyllosilicates have sorption properties useful for SOx abatement.. Since such phyllosilicate materials are stable in the crystalline oxide structure and essentially reversible in sorbent properties up to about 400°C, stable sorbent may be employed in moderately elevated industrial processes, such as cold side combustion effluent treatment of fossil fuel burning power plants. Natural chlorites containing up to 30 weight percent MgO are known, with those containing about 14 to 29 wt% MgO being preferred.

In a preferred embodiment of the invention, a novel process of sulfur oxide sorption is provided, wherein a gas containing sulfur oxide is contacted at process temperature at elevated temperature, from about 200°C up to about 750°C, with a solid phyllosilicate sorbent material to remove sulfur oxide from the gas. A preferred solid phyllosilicate sorbent material comprises alternating silicate layers and layers having a brucite crystalline structure containing divalent and trivalent metal oxides comprising predominantly magnesia and alumina present in the brucite structure. The amount of phyllosilicate in the solid sorbent can vary from about 10 to 100 wt%. A

preferred sorbent composition comprises a mixture of 10 to 90 parts by weight of magnesia-rich chlorite containing about 10-30 weight percent MgO and 10 to 90 parts by weight of hydrotalcite containing at least 50 weight percent MgO.

Sulfur oxide sorption and/or release may be enhanced by depositing on solid sorbent material an effective amount (~~eg- 50 to 500 ppm~~) of metal oxide, such as cerium, vanadium and/or platinum. ✓

The invention also provides processes for reducing the amount of SOx emissions passing through a fluidized particle bed (eg-FCC petroleum refining) or in fossil fuel combustion, such as cold side coal combustion processes.

DETAILED DESCRIPTION OF THE INVENTION

In the following description, units are given as parts by weight and metric units unless otherwise indicated.

The chlorite group is often not considered a part of the clays and is sometimes left alone as a separate group within the phyllosilicates. It is a relatively large and common group although its members are not well known. Some of the recognized members include: Amesite, Baileychlore, Chamosite, Clinochlore, Cookeite, Corundophilite, Gonyerite, Nimite, Odinite, Orthochamosite, Penninite, Pannantite, Rhipidolite, (prochlore), Sudoite, and Thuringite. The term chlorite is often used to denote any member of this group when differentiation between the different members is not possible. The general formula is $X_{4-6}Y_4O_{10}(OH, O)_8$. The X represents either aluminum, iron, lithium, magnesium, manganese, nickel, zinc or rarely chromium. The Y represents either aluminum, silicon, boron or iron but mostly aluminum and silicon.

The gibbsite layers found in conventional clay groups are replaced in the chlorites by a similar layer that is analogous to the oxide brucite. The structure of this group is composed of silicate layers sandwiching a brucite or brucite-like layer in between, in an s-b-s stacking sequence similar to the above groups. However, in the chlorites, it is believed that there is an extra weakly bonded brucite layer in between the s-b-s sandwiches. This gives the structure an s-b-s b s-b-s b sequence. Variable amounts of water molecules can be between the s-b-s sandwiches and the brucite layers. ✓

Manufacturing Processes-

The manufacturing materials and methods useful in practicing this invention are typically disclosed in U.S. Patent No. 5,928,496 (Albers et al) and PCT Publication No. WO 99/19251, incorporated herein by reference.

The magnesia-rich contact solids made by this invention may be self-bound or may include a binder component to hold the inorganic compounds together into the desired shape, such as spheroidal particles. Depending on the application, different binding systems are used, and binders may be added to milled metal oxides/salts prior to forming the aqueous slurry. For example, in more severe high temperature applications such as fluid cracking catalyst (eg- 700-820°C), a hydrothermally stable inorganic binder such as aluminum chlorohydrate or peptized alumina is used. Effective inorganic binders include sols of aluminum such as aluminum chlorohydrate, peptized aluminas, sols of silica, colloidal silicas, sols of titanium, sols of zirconium clays such as bentonite, calcined kaolinite, kaolinite, metakaolin, montmorillonite, low-magnesia chlorite talc, and mixtures of these. Desirable inorganic binders include a sol of aluminum, peptized alumina, a sol of silica, colloidal silica, a sol of titanium, a sol of zirconium, a clay, and mixtures thereof.

Slurry Techniques – Finely-divided milled solids components are mixed with water, preferably containing about 0.1 to 1 wt% surfactant comprising acid stable fluorohydrocarbon prior to forming and drying the contact solids product herein. It may be advantageous to provide pre-blended, dry-milled materials for dispersion in water and spray dried or otherwise manufactured as dry particles in a short time period. Hydrolyzable metal oxides and salts are advantageously pre-blended and stored in the substantial absence of added water. Batch or continuous inline feeding of slurry components is well known. Thereafter, the slurry is pumped or otherwise transported to the spray dryer feed tank.

It is a significant advantage to use limited amounts of water in forming a fluent slurry for spray drying. By decreasing the amount of water below a weight ratio of 2:1 water:solids (ie - typically 30 wt% or more solids), energy savings are realized in the drying step. By maintaining effectively dry solids in admixture before forming the slurring within, for instance one hour before drying, surface hydrolysis is avoided or minimized.

In the preferred methods, a suitable alkaline stable or acid stable surfactant is added to the slurry. Surfactants for improving the physical and catalytic properties of FCC catalysts are disclosed in US Patent 5,330,943 (Shi et al). Improved attrition resistance and standard testing (ie- Attrition Index or 'AI') are described by Shi et al, who recommend about 0.25-4 grams per 5 kg of spray dried product. Preferred acid stable surfactants are fluorohydrocarbons manufactured under the trade name "DuPont Zonyl TBS" or 3M "FC-95", and 0.01-1 wt % is satisfactory. The use of surfactant is believed to contribute to attrition resistance by decreasing the 'blow holes' during spray drying.

Spray Drying - Conventional spray drying techniques are known to the industry, usually withdrawing a slurry containing sufficient water to form a fluent mixture of solids and liquid phases, advantageously incorporating a surfactant to impart homogeneity and mechanical properties to the resulting dry products. Heat and low pressure permit flashing or rapid evaporation of the liquid phase from a slurry mist, resulting in agglomeration of smaller particles to form larger solid, typically having a spheroidal shape and a particles size distribution in the 20-250 micron (μ) range or larger. In the manufacture of FCC catalyst or additive solids, the particles typically have an average size of 20-100 μ . In sorbent particles for fluid bed processes, a larger particle having an average size of about 150-200 μ may be desired.

The phyllosilicate sorbent composition may include a combination of inorganic oxides with an inorganic binder, an organic binder, or a mixtures of an inorganic and organic binder. Desirable inorganic oxides include a member selected from the group consisting of oxides or hydroxides of aluminum, calcium, cobalt, copper, iron, magnesium, molybdenum, silicon, titanium, vanadium, zinc, tungsten, strontium, nickel, manganese, zirconium, barium, members of the lanthanide series and mixtures thereof. Synthetic hydrotalcites having a large MgO content (preferably about 50-70 wt%) are particularly suitable for use as SO_x sorbents.

The contact solid composition may be self-bound or may include a binder component to hold the inorganic oxides together into the desired shape, such as spheroidal particles. Depending on the application, different binding systems are used. For example, in more severe high temperature applications such as fluid cracking catalyst (eg- 700-820 C), a hydrothermally stable inorganic binder such as aluminum chlorohydrol or peptized alumina is used.

Effective inorganic binders include sols of aluminum such as aluminum chlorohydrol, peptized aluminas, sols of silica, colloidal silicas, sols of titanium, sols of zirconium clays such as bentonite, calcined kaolinite, kaolinite, metakaolin, montmorillonite, chlorite, talc, and mixtures of these. Desirable inorganic binders include a sol of aluminum, peptized alumina, a sol of silica, colloidal silica, a sol of titanium, a sol of zirconium, a clay, and mixtures thereof.

The smectite clays are especially desirable alone or in combination with zinc oxide/titania mixtures, various inorganic binders and smectite. In some applications, such as a fluidized or ebullating bed, found in many flue gas desulfurization units, an organic binder such as hydroxypropyl methyl cellulose or polyvinyl alcohol is used.

Other components can be added to the catalyst composition to enhance the performance of conversion catalyst in specific applications or for a specific set of operating conditions. An oxidation promoter such as platinum or cerium can be added to the catalyst solids to facilitate the oxidation of

SO₂ to SO₃, for instance in the fluid cracking catalyst regenerator, thus improving the overall performance of the catalyst. Desirable additional components can include any number of activators, promoters, oxidizers, reducers, scavengers, and mixtures of these components. These materials may enhance performance. The solid composition preferably is prepared in the form of a spheroidal particle of about 1 to 10,000 microns diameter.

Sorption Process Applications: - The present invention provides suitable magnesia-rich sorbents for fluidizable catalysts or contact solids, methods for using such materials to reduce the emissions of sulfur compounds from industrial processes, and methods for preparing such contact solids or catalysts. The conversion, processing or burning of sulfur-containing fossil fuels can result in the emission of sulfur-containing compounds, such as H₂S and SO_x, to the atmosphere. To comply with increasingly stringent environmental regulations, materials are sought to reduce the emissions of sulfur compounds from industrial processes. Several methods of desulfurization are currently being used commercially. These methods include flue gas scrubbing as well as various fixed bed, ebullating bed, and fluid bed catalytic reaction processes. Some of these processes treat the flue gas just prior to the release of gas to the atmosphere.

Other processes are performed upstream of the emission release in order to prevent the undesired emission from occurring. The goal of such processes is to reduce emission of sulfur-containing compounds into the atmosphere.

The inventive process reduces the amount of SO_x emissions passing through a fluidized particle bed. This process may comprise the step of introducing into the fluid particle bed a microspheroidal catalyst having a composition comprising at least 10 wt% of SO_x-capturing MgO-rich chlorite-type phyllosilicate. Typically, this involves sorbing or capturing SO₃ in the fluid particle bed regenerator as an inorganic sulfate in a fluid cracking catalytic operation. In a petroleum refinery SO_x emissions are often generated in the fluid cracking catalyst regenerator and released in its flue gas.

A typical sulfur abatement process includes the step of introducing into the fluid particle bed a microspheroidal catalyst having a composition comprising at least one SO_x-capturing oxide and at least one inorganic binder. Oxidation of SO₂ to SO₃ can be achieved employing an oxidation promoter catalytic component in a fluid particle bed, such as FCC regenerator.

The capture of SO₃ in the fluid particle bed regenerator as an inorganic sulfate on the SO_x-capturing oxide is usually followed by reducing the inorganic sulfate to a sulfide in a fluid particle bed reactor/stripper. Then, the sulfur can be released as H₂S upon hydrogenolysis or reduction in the

stripper. Incorporation of a minor amount of a vanadium oxide component in the contact solids promotes reduction of sulfate during regeneration of the sorbent.

The catalyst composition is desirably formed into a fluidizable particle having an average particle size in the range of about 20 μ -300 μ that is useful in both conventional fluidized bed and ebullating bed processes. The SO_x-capturing oxide of the invention is desirably a magnesia-rich solid and/or mixed inorganic oxide additive for catalyzing the capture and release of sulfur-containing compounds in the fluid cracking catalyst. This provides refiners with an effective means for reducing fluid cracking catalyst SO_x emissions. The invention provides a contact solids or catalyst composition employed as a formed spheroidal catalyst that reduces the emissions of sulfur containing compounds from industrial processes. For example, in the preferred embodiment of the invention, the MgO-rich phyllosilicate captures and thereby removes the sulfur containing species, such as H₂S or SO_x that is present in the gas stream being treated. Advantageously, this invention is employed to reduce emissions of sulfur compounds from a fluid cracking catalyst (FCC) process. Particulate solids are added to the FCC unit in the same manner as the conventional cracking catalyst (eg- REY zeolite). The magnesia-rich brucitic additive can be introduced separately or together in a mixture with the cracking catalyst. Usually the addition is accomplished by a pneumatic conveying system to blow the material directly into the FCC catalyst regenerator. The catalyst additive then circulates through the fluid cracking catalyst unit in direct contact and along with the fluid cracking catalyst. The quantity of fluid cracking catalyst additive that is added and which then circulates in the unit is sufficient to effectively reduce the emissions of sulfur containing compounds from the FCC unit, yet it need not be present in a proportion so large that it deleteriously affects the operation of the cracking process reactions. Fluid cracking catalyst additive level of between about 0.5 and about 10 weight percent of the circulating fluid cracking catalyst inventory is desirable.

Industrial processes for sulfur oxide abatement may be conducted at various temperatures. In the coal gasification process, the flue gas or hot gas is passed through a fluidized or ebullating bed of catalyst to remove sulfur compounds. Whereas cold side flue gas abatement may be carried out advantageously at about 200° to 400°C, more elevated temperatures in the 400° to 700°C range may be employed. FCC processes may employ the sorbents at 700° to 820°C or higher temperature, as will be understood by the skilled chemical engineer.

Sulfur Oxide Sorption Testing -

A standard test method for measuring such sorption characteristics is thermogravimetric analysis (TgA), wherein a test sample of the crystalline solid material is heated at predetermined rate

to 700 C, releasing water of hydration. A gaseous stream containing the sulfur oxide is then contacted with the sample and weight of sorbed material is measured. Regeneration of the sorbent (ie- by reduction of sulfate to sulfite) can be effected by passing a hot gas, such as hydrogen over the sample.

In the following examples, various contact solids test by TgA for comparing SOx sorption in a controlled heating, sorption and regeneration cycle. A standard duPont TgA unit is employed to test samples in the TgA ramp method. The sample is heated at uniform rate to 700° C with a flowing stream of nitrogen through the sample. The sorption cycle employs 3000 ppm. SO₂ in a carrier gas stream containing 3 wt% oxygen and balance nitrogen and maintains the sample at predetermined temperature of 700° C for at least 30 minutes during sulfur oxide sorption. Regeneration is performed by hot hydrogen gas flowing over the sample at 650° C.

Typical naturally-occurring minerals having a chlorite structure are given in the following tables.

Table 1 – Amesite.

Chemical Formula:	Mg ₂ Al(SiAl)O ₅ (OH) ₄			
Composition:	Molecular Weight = 278.68 gm			
	<u>Magnesium</u>	17.44 %	Mg	28.92 % MgO
	<u>Aluminum</u>	19.36 %	Al	36.59 % Al ₂ O ₃
	<u>Silicon</u>	10.08 %	Si	21.56 % SiO ₂
	<u>Hydrogen</u>	1.45 %	H	12.93 % H ₂ O
	<u>Oxygen</u>	51.67 %	O	
		100.00 %		100.00 % = TOTAL OXIDE
Empirical Formula:	Mg ₂ Al ₂ SiO ₅ (OH) ₄			

Table 2 – Chamosite

Chamosite	(Fe ⁺⁺ ,Mg,Fe ⁺⁺⁺) ₅ Al(Si ₃ Al)O ₁₀ (OH,O) ₈			
Chemical Formula:				
Composition:	Molecular Weight = 660.15 gm			
	<u>Magnesium</u>	5.52 %	Mg	
	<u>Aluminum</u>	8.17 %	Al	
	<u>Iron</u>	29.61 %	Fe	
	<u>Silicon</u>	12.76 %	Si	
	<u>Hydrogen</u>	0.31 %	H	
	<u>Oxygen</u>	43.63 %	O	
		100.00 %		
Empirical Formula:	Fe ²⁺ ₃ Mg _{1.5} AlFe ³⁺ _{0.5} Si ₃ AlO ₁₆ (OH) ₂			

Table 3 –Orthochamosite

Chemical Formula:	(Fe ⁺⁺ ,Mg,Fe ⁺⁺⁺) ₅ Al(Si ₃ Al)O ₁₀ (OH,O) ₈			
Composition:	Molecular Weight = 664.18 gm			
	<u>Magnesium</u>	5.49 %	Mg	9.10 % MgO

<u>Aluminum</u>	8.12 %	Al	15.35 %	Al ₂ O ₃	
<u>Iron</u>	29.43 %	Fe	32.45 %	FeO /	6.01 % Fe ₂ O ₃
<u>Silicon</u>	12.69 %	Si	27.14 %	SiO ₂	
<u>Hydrogen</u>	0.91 %	H	8.14 %	H ₂ O	
<u>Oxygen</u>	43.36 %	O			
	100.00 %		98.19 %	= TOTAL OXIDE	

Empirical Formula: $\text{Fe}^{2+}_3\text{Mg}_{1.5}\text{Fe}^{3+}_{0.5}\text{Al}_2\text{Si}_3\text{O}_{12}(\text{OH})_6$

Table 3 - Clinochlore (kaemmererite)

Chemical Formula: $(\text{Mg},\text{Fe}^{++})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$

Composition: Molecular Weight = 595.22 gm

<u>Magnesium</u>	15.31 %	Mg	25.39 %	MgO	
<u>Aluminum</u>	9.07 %	Al	17.13 %	Al ₂ O ₃	
<u>Iron</u>	11.73 %	Fe	15.09 %	FeO	
<u>Silicon</u>	14.16 %	Si	30.28 %	SiO ₂	
<u>Hydrogen</u>	1.35 %	H	12.11 %	H ₂ O	
<u>Oxygen</u>	48.38 %	O			
	100.00 %		100.00 %	= TOTAL OXIDE	

Empirical Formula: $\text{Mg}_{3.75}\text{Fe}^{2+}_{1.25}\text{Si}_3\text{Al}_2\text{O}_{10}(\text{OH})_8$

Table 4 - Gonyerite

Composition: Molecular Weight = 703.49 gm

<u>Magnesium</u>	10.36 %	Mg	17.19 %	MgO	
<u>Manganese</u>	23.43 %	Mn	30.25 %	MnO	
<u>Iron</u>	9.53 %	Fe	13.62 %	Fe ₂ O ₃	
<u>Silicon</u>	15.17 %	Si	32.46 %	SiO ₂	
<u>Hydrogen</u>	0.57 %	H	5.12 %	H ₂ O	
<u>Oxygen</u>	40.94 %	O			
	100.00 %		98.64 %	= TOTAL OXIDE	

Empirical Formula: $\text{Mg}_3\text{Mn}^{2+}_3\text{Fe}^{3+}\text{Si}_{3.8}\text{Fe}^{3+}_{0.2}\text{O}_{14}(\text{OH})_4$

Table 4 - Nimite

Chemical Formula: $(\text{Ni},\text{Mg},\text{Fe}^{++})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$

Composition: Molecular Weight = 666.98 gm

<u>Magnesium</u>	6.19 %	Mg	10.27 %	MgO	
<u>Aluminum</u>	8.09 %	Al	15.29 %	Al ₂ O ₃	
<u>Iron</u>	5.86 %	Fe	3.23 %	FeO /	4.79 % Fe ₂ O ₃
<u>Silicon</u>	12.63 %	Si	27.03 %	SiO ₂	
<u>Nickel</u>	22.88 %	Ni	29.12 %	NiO	
<u>Hydrogen</u>	1.16 %	H	10.40 %	H ₂ O	
<u>Oxygen</u>	43.18 %	O			

100.00 % 100.12 % = TOTAL OXIDE

Empirical Formula: $\text{Ni}_{2.6}\text{Mg}_{1.7}\text{AlFe}^{3+}_{0.4}\text{Fe}^{2+}_{0.3}\text{Si}_3\text{AlO}_{10.3}(\text{OH})_{7.7}$

Table 5 - Sudoite

Chemical Formula:	$\text{Mg}_2(\text{Al}, \text{Fe}^{+++})_3\text{Si}_3\text{AlO}_{10}(\text{OH})_8$				
Composition:	Molecular Weight = 546.77 gm				
	<u>Magnesium</u>	8.45 %	Mg	14.01 %	MgO
	<u>Aluminum</u>	19.25 %	Al	36.36 %	Al_2O_3
	<u>Iron</u>	3.06 %	Fe	1.31 %	FeO / 2.92 % Fe_2O_3
	<u>Silicon</u>	15.41 %	Si	32.97 %	SiO_2
	<u>Hydrogen</u>	1.46 %	H	13.01 %	H_2O
	<u>Oxygen</u>	52.38 %	O		
		100.00 %		100.59 %	= TOTAL OXIDE
Empirical Formula:	$\text{Mg}_{1.9}\text{Fe}^{2+}_{0.1}\text{Al}_{2.9}\text{Fe}^{3+}_{0.2}\text{Si}_3\text{AlO}_{10}(\text{OH})_{7.9}$				

In addition to the desired chlorite-type materials, magnesia-rich hydrotalcite containing about 50-70% MgO are excellent SO_x sorbents, alone or in combination with other materials. As an example of suitable synthetic HTC (Sasol "PURAL MG 70") is provided, as described in the following Table.

Table 6 - Hydrotalcite -(HTC)

HTC			
Composition:	<u>Magnesium</u>	70.8 %	MgO
	<u>Aluminum</u>	29.2 %	Al_2O_3
Surface Area	201. m ² /g		
Particle size	<25 micron	59.2%	
	<45 "	92.9%	
	<90 "	100%	
Size at 50%	21.6 micron		
Bulk Density	0.59g/ml.		

Sorption Examples:

Example 1 - A standard TgA SO₂ sorption test is run with an admixture of 60 parts by weight of Luzenac chlorite (30 wt% MgO) and 40 parts inert solids (Thiele RC-87 kaolin clay), to which is added 12 parts cerium oxide and 2 parts vanadium pentoxide. The test sample had an average particle size of about 2-10 microns. TgA preheat cycle of about 38 minutes reduced the standardized sample from 100 weight units to about 92 units, probably due to dehydration. SO_x sorption at 70 minutes increased the sample to about 95.5 units, and hot hydrogen desorption further reduced the sample to 89 weight units. The same sample was subjected to a second sorption cycle, which provided increased sorption from the standardized 100 units to about 106 units. Although the mechanism for increased sorption capacity with recycle is not fully understood, it is clearly demonstrated that solid sorbent is regenerated with hot hydrogen and recycled, thereby enhancing sulfur oxide sorption properties

Example 2 - The above example 1 is repeated with a mixture of 20 parts by weight of the magnesia-rich chlorite, 50 parts of "Pural MG 70" hydrotalcite, 30 parts kaolin, and the same amounts of cerium and vanadium additives. TgA preheat cycle of about 34 minutes reduced the standardized sample from 100 weight units to about 98 units. SOx sorption at 50 minutes increased the sample to about 114 units, and hot hydrogen desorption further reduced the sample to about 95 weight units. The mixture of two magnesia-rich components appears to have greater SOx sorption capacity than would be expected from each component acting alone.

Example 3 - The above example 1 is repeated with a mixture of 60 parts by weight hydrotalcite, 40 parts kaolin, and the same amounts of cerium and vanadium additives. TgA preheat cycle of about 30 minutes reduced the standardized sample from 100 weight units to about 95 units. SOx sorption at 60 minutes increased the sample to about 114 units, and hot hydrogen desorption further reduced the sample to about 93 weight units.

According to the present invention, it is advantageous to employ solid sorbent material comprising at least one layered magnesia-rich containing layers of brucite structure, wherein the brucite material is predominately magnesia, having an average MgO content of at least 50wt%, particularly wherein the sorbent comprises a mixture of magnesia-rich chlorite and hydrotalcite in a weight ratio of about 10:90 to 90:0 chlorite:hydrotalcite.

While the invention has been shown and described by particular examples, there is no intent to limit the inventive concept except as in the following claims.